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Applicant: Richard W. Strobel
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Examiner: John J. Zimmerman
Art Unit: 1775

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DECLARATION OF KRYSTYN J. VAN VLIET

I, KRYSTYN J. VAN VLIET, do hereby declare that:

1.   I am currently employed as an Assistant Professor of Materials Science and Engineering at the Massachusetts Institute of Technology (MIT). I have expertise in the area of metal coatings including techniques used to characterize properties (e.g., hardness) of such coatings.

2.   I have the following degrees: Sc.B. in Materials Science and Engineering, Brown University (1998); Ph.D. in Materials Science and Engineering, Massachusetts Institute of Technology (2002).

3.   Prior to being employed by MIT, I worked at Children's Hospital Boston as a Postdoctoral Fellow.

4.   I have published a number of technical papers related to nanoindentation hardness measurements including those set forth in Appendix A.

5.   I have reviewed the patent application bearing serial no. 09/991,287, entitled TIN-SILVER COATINGS, by Richard W. Strobel (hereinafter "the Patent Application"); the office action mailed June 16, 2004 in connection with the Patent Application; and, the references relied upon by the Examiner including U.S. Patent No. 5,075,175 (hereinafter "Brinkmann patent").

6.   The specification of the Patent Application provides sufficient detail such that the following would be clearly understood by those of ordinary skill in the art upon review of the Patent Application:

     (1) the meaning of "nanoindentation hardness,"

(2) the meaning of the units "GPa" (gigapascal) used in connection with the nanoindentation hardness results, and

(3) details of parameters used in obtaining the nanoindentation hardness results sufficient to enable reproduction of the invention and comparison of the processes and products of the invention to processes and products of others,

Details relevant to these statements are provided in the paragraphs below.

7.   Based on experimental testing which I carried out personally, using my knowledge of the art and parameters accepted by those of ordinary skill in the art, I have concluded that the materials described and claimed in the Patent Application have a significantly higher nanoindentation hardness than materials described in Brinkmann. Details of this are outlined in the paragraphs below.

8.   It is a well-established metallurgical principle known to those of ordinary skill in the art that processing affects microstructure, and that microstructure in turn affects properties. Electroplated coatings have a different microstructure than non-electroplated coatings. Furthermore, one of ordinary skill in the art would be able to distinguish an electroplated coating from a non-electroplated coating by examining the microstructure of the coatings.

9.   Although there is overlap between the claimed material compositional ranges of the Patent Application and the broadest ranges disclosed by Brinkmann, Brinkmann points, through his examples and description, in a direction different from the ranges claimed in the Patent Application.

The materials described in Brinkmann's examples include, at most, a silver content of 1% (Example 1). It is a stated goal of Brinkmann to keep the materials' melting temperature as low as possible (see, e.g., Column 2, lines 33-35 of Brinkmann) which increases the solderability of the material (a further stated goal of Brinkmann, e.g., See Column 2, lines 46-47). At the time of the filing of Brinkmann, soldering was required to connect components, as described by Brinkmann, to other components to form a functional device, thus it was desired to keep the material's melting temperature as low as possible. Additionally, those of ordinary skill in the art would understand that other manufacturing complications can exist with higher melting point materials.

Increasing the silver content of Brinkmann's material to the ranges claimed in the Patent Application (e.g., from 3% to 20%) would increase the melting point of the Brinkmann material. Therefore, Brinkmann's disclosure, as a whole, would be understood by those of ordinary skill in the art to teach away from a silver content higher than that of the working examples (1%) and the claimed silver content ranges.

10.   There is no express teaching in Brinkmann (or any of the prior art relied upon in the office action) that increasing silver content of the alloys described in Brinkmann would in any way increase hardness. Nor would those of ordinary skill in the art be able to infer any implied or inherent teaching in Brinkmann (or any of the prior art relied upon in the office action) that increasing silver in such an alloy would increase hardness.

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One feature of the Patent Application is the discovery that one can increase nanoindentation hardness as silver content of a silver-tin alloy increases.

11.   One of ordinary skill in the art would understand that nanoindentation is a known technique for measuring hardness and that "nanoindentation hardness" refers to the hardness determined from nanoindentation experiments. Nanoindentation was developed in the late 1980s to facilitate mechanical testing of coatings on substrates, enabling distinction of coating properties independent from substrate properties.

Those of ordinary skill in the art understand that nanoindentation involves applying a force to a sample with an indenter, using parameters as described below in paragraph 13. During nanoindentation, the applied force is measured simultaneously with indenter displacement to provide load-displacement experimental data from which nanoindentation hardness is calculated.

Nanoindentation hardness is representative of the average pressure the material can sustain beneath the indenter. Therefore, as known to those of ordinary skill in the art, the units for nanoindentation are expressed in MKS units of pressure, such as GPa. Where nanoindentation hardness is described in units of GPa, as in the Patent Application, those of ordinary skill would understand that experimental data is converted to hardness in GPa units via analysis of standard units of load per unit area, representing the maximum applied load normalized by the concurrent projected area of the indentation formed in the metal surface, calculated according to Oliver and Pharr (1992) Method of Instrumented Nanoindentation Data Analysis.

12.   Nanoindentation is a superior technique for measuring the hardness of the metal alloy coatings described in the Patent Application than conventional microhardness testing techniques (such as Brinell, Rockwell, Vickers and Knoop diamond indentation). Force and displacement can be measured at significantly greater resolution (e.g., microNewtons and nanometers, respectively) using nanoindentation compared to the microhardness techniques and, thus, provides a more accurate evaluation of hardness. Moreover, the loads required to meet American Society of Testing and Materials (ASTM) standards of microhardness testing would result in an indentation depth that would exceed the thickness of the metal alloy coatings described in the Patent Application and/or exceed the depth to which substrate effects on calculated hardness are minimized.

13.   One of ordinary skill in the art understands that nanoindentation of a thin metal coating on a substrate, such as described in the Patent Application, uses standard measurement parameters that do not need to be further qualified or described beyond the description in the Patent Application. These standard parameters include: use of a Berkovich-type pyramidal three-sided sharp indenter; use of an appropriate maximum indentation depth selected to minimize effects from the substrate (e.g., less than 33% of the coating thickness as described in the Patent Application); and, measuring a sufficient number of samples to provide a standard deviation of less than 10%.

One of ordinary skill in the art would also understand that there is no need to provide the maximum load as a parameter for nanoindentation because load and

displacement are measured simultaneously throughout the technique, as noted above in Paragraph 11.

14. One of ordinary skill in the art understands that nanoindentation uses standard sample preparation techniques for measuring metal alloy coatings (such as those described in the Patent Application) that do not need to be further qualified or described beyond the description in the Patent Application. Metal alloy coatings formed in a dipping process (such as those described in the Patent Application) are evaluated without polishing or other special preparation. That is, there would be no need to polish the sample prior to indentation testing. Since dip coating results in a smooth surface that does not require polishing, those of ordinary skill in the art would understand that, without further qualification or description, the procedure as outlined in the Patent Application would not involve polishing prior to testing, and that this would result in a more realistic hardness determination, rather than one that might otherwise be artificially increased in hardness due to surface preparation.

15. Therefore, one of ordinary skill in the art would understand, without further qualification or description, how the nanoindentation hardness values disclosed and claimed in the Patent Application were determined and what the values represented.

16. I used the nanoindentation techniques following the standard parameters described above to evaluate the hardness of the metal alloy coatings described in the Patent Application (August 2001); metal alloy castings of the composition described in Example 1 of the Brinkmann patent (July 2003); and metal alloy coatings of the compositions described in Example 1 of the Brinkmann patent (February 2004). The metal alloy coatings described in the Patent Application (August 2001) that I evaluated included:

      100% Ag;

      Sn-x% : Ag (where x = 2, 5, 10)

The metal alloy compositions described in Example 1 of the Brinkmann patent that I evaluated included:

      Sn-1%: Ag : P - .03%

The testing of the castings (July 2003) provided an initial comparison to the metal alloy coating compositions of the Patent Application. The testing of the coatings (February 2004) was conducted at the request of the Examiner to provide a more relevant comparison to the metal alloy coatings of the present invention.

17. The casting surface was prepared through low grit grinding and polishing due to the fact that the surface roughness of the casting was greater than the intended indentation depth of 1 micron. As noted above, the coating surfaces were not polished (or otherwise prepared) because the surface roughness of the coatings was sufficiently low and because it was desirable to maintain maximum coating thickness to mitigate substrate artifacts. It is well-known that polishing of metal surfaces results in slight increases in calculated hardness with respect to smooth, unpolished surfaces because polishing increases defect density at the metal surface.

18.   Although I used a different nanoindentation instrument to evaluate the coatings described in the Patent Application (in August 2001) than I did to evaluate the compositions described in the Brinkmann patent (July 2003 and February 2004), I have confirmed through use of these two instruments over the past four years that upon proper calibration of these instruments against force and material standards (as is my practice), calculated nanoindentation hardness is not instrument-dependent.

19.   Figure 1 compares the nanoindentation hardness for each of the samples I examined using nanoindentation, where results are reported in units of Pascals as discussed above. Clearly, nanoindentation hardness increases as a function of wt% Ag in the binary Sn-x% : Ag, x = 2 – 10 wt% coatings.
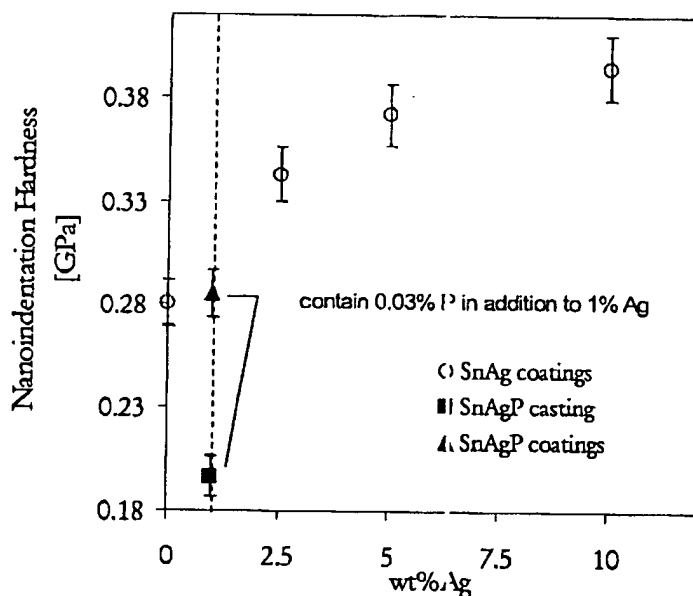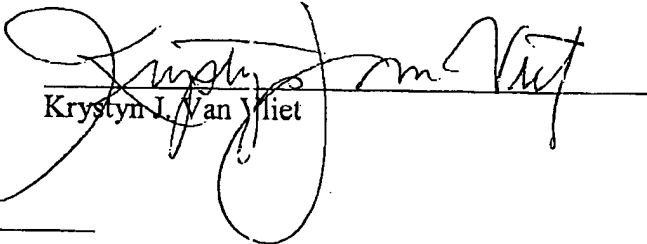

Figure 1. Nanoindentation hardness as a function of alloy composition. Note that filled symbols represent alloys containing 0.03% P in addition to 1% Ag.

20.   The Brinkman coating and casting compositions exhibited respective nanoindentation hardnesses of 0.28 GPa and 0.20 GPa . The nanoindentation hardness for the casting and coating compositions were also lower than that predicted by interpolation of the compositions described in the Patent Application, which can be represented as a power-law increase in hardness with wt% Ag. A Sn-1% : Ag coating of the Patent Application should result in nanoindentation hardness of 0.32 GPa. The nanoindentation hardnesses of the Brinkman casting and coating compositions were are 13% and 65% lower, respectively, than the data for coating compositions described in the Patent Application would predict.

21. Based on the data of the tests I performed, I conclude that:

1. The Brinkmann coating composition (Sn-1%: Ag: 0.03%P) has a nanoindentation hardness significantly lower than the nanoindentation hardness values claimed in the Patent Application (i.e., 0.32 to 0.41 GPa).
2. The Brinkmann coating composition (Sn-1%: Ag: 0.03%P) exhibits a statistically significant decrease in hardness of 13% when compared the data predicted for Sn-1%: Ag coating compositions described in the Patent Application.
3. The differences in hardness between the Brinkmann coating composition and the coating compositions of the Patent Application are, in my opinion, due to differences in composition and/or microstructure.
4. The mechanical properties of the substrates did not affect the calculated nanoindentation hardness of the coatings tested including the Sn-Ag coatings and the Sn-Ag-P coatings.

22. I conclude based on my review of the Brinkmann patent that P is added intentionally to metal coatings to reduce oxidation and/or to lower the melting point. Although the amount of P in the Brinkmann coating is low, the P was added intentionally as a deoxidizing agent and/or melting temperature depressant, for the following reasons:

1. The abstract of this patent specifically notes the inclusion of "small amounts of deoxidation and processing additives" [my emphasis], which is distinct in the field of metallurgy from impurity elements.
2. Claim 4 indicates intentional inclusion in the Sn alloy of "up to 0.5% by weight of material from the group consisting of zinc, phosphorous, and mixtures thereof", and these two elements serve similar metallurgical purposes in molten baths of low melting alloys.
3. The alloy discussed in Example 1 distinguishes the alloy composition "containing 1% by weight of silver and 0.03% by weight of phosphorous" from the "remainder of the alloy...made up of tin and unavoidable impurities", indicating clearly that P was not considered by the inventor as an unavoidable impurity.
4. Example 2 also specifically indicates addition of "0.02% by weight of phosphorous" among other alloying elements, and does not specifically indicate consideration of impurity elements.
5. A survey of several ASTM standards of chemical composition and impurity element concentration for Sn-x%Ag, x <10 wt% alloys including ASTM B32 GradeSn95 (Sn-5wt% Ag) and Class 96 TS (Sn-4wt%Ag) indicates that P is not considered a typical impurity element in Sn-Ag alloys that must be regulated to specific levels.

23. It is a well-established metallurgical principle known to those of ordinary skill in the art that composition and processing affect microstructure, and that microstructure in turn affects properties. For example, it is well-established that, for a fixed composition and melt temperature, a bulk casting will have significantly greater grain size than a metal substrate-dipped coating because of the relatively slower cooling rate of the casting, and will thus have a plastic mechanical properties and hardness which are

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significantly lower than those of the coating. It is therefore not surprising that the Sn-1%Ag-0.03%P casting has hardness that is 30% lower than that of a coating of the same melt composition. Likewise, different coating processes (e.g., melt dipping vs. electroplating) will produce distinct microstructures and thus distinct mechanical properties, even for a fixed alloy composition. For constant processing conditions, the addition of P may cause a decrease in hardness because it also causes changes to the final microstructure; at the reported concentration of 0.03%, this is most likely due to change in grain size and distribution of Ag within the Sn-matrix.

24.   The undersigned declares further that all statements made herein of her own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Krystyn J. Van Vliet

Date: 12/06/04

Serial No. 09/991,287
Conf. No. 3691

Art Unit: 1775

APPENDIX A

1.   "Atomistic Mechanisms Governing Elastic Limit and Incipient Plasticity in Crystals," J. Li et al, *Nature* 418:307-310 (2002).

2.   "Direct Measurement of Indentation Frame Compliance," K. Van Vliet et al., *J. Mater. Res.* 19(1):325-331 (2004).

3.   "Size Effects on the Onset of Plastic Deformation During Nanoindentation of Thin Films and Patterned Lines," Y. Choi et al., *J. App. Physics* 94(9):6050-6058 (2003).